Polyester Resin Coatings as Barrier Against Aggressive Agents. Influence of Volumetric Pigment Concentration

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Abstract
In this paper we present experimental results of electrochemical measurements (EIS and anodic polarization) on the performance of polyester copolymers films obtained at the various volumetric pigment content (VPC).

Introduction
Polymer films could restrain the aggressive action of water and oxygen and act as a barrier against aggressive agents.
The performance of polymer films shows as a barrier against corrosive agents and depends on the polymer structure, the thickness and degree of adhesion to the metal substrate, the nature of metallic substrate [1]. Electrochemical techniques are usually used to evaluate the corrosion behavior of organic coatings. EIS is a non-invasive method and allows the determination of both the dielectric properties of organic coatings and corrosion processes at the interface metal / organic film [3, 4]. The protective properties of the organic film can be increased by use of anticorrosive pigments. The performance of a coating can be evaluated from electrochemical techniques [2].

Experimental
The protective coatings were obtained from polyester resins with ZnO pigment on iron substrate. Four types of resin are used: R1 fat alkyd; R2 medium alkyd, modified with aromatic polyurethane; R3 medium alkyd, modified with styrene and R4 medium alkyd, modified with aliphatic polyurethane. From each type of resin four formulations are prepared with different volumetric pigment content (**Table 1**).
Properties of the coatings were investigated by electrochemical impedance spectroscopy (EIS) and polarization experiments in 3% NaCl solution.
Before each measurement the iron electrode was carefully polished mechanically with SiC paper and spray with different degrees of diamond abrasive to mirror-surface (glossy).
EIS measurements were performed using FRA AUTOLAB 302N module in the frequency range of 0.1 Hz to 100 kHz and an amplitude AC voltage of 10 mV with. Each spectrum was collected containing 60 points with a logarithmic distribution of 10 points per decade. Experimental electrochemical impedance data were modeled using an equivalent electrical circuit by Levenberg-Marquardt CNLS procedure using the software-Scribner Associates Inc. Zview.

Table 1. Characteristic of prepared coatings

No.	Code sample	Resin type	VPC*, %
1	V1	R1 fat alkyd	64.69
2	V2		44.16
3	V3		25.70
4	V4		15.09
5	V5	R2 medium alkyd, modified with aromatic polyurethane	36.89
6	V6		3.3
7	V7		16.58
8	V8		16.22
9	V9	R3 medium alkyd, modified with polystyrene	75.80
10	V10		47.10
11	V11		28.53
12	V12		17.07
13	V13	R3 medium alkyd, modified with aliphatic polyurethane	42.49
14	V14		27.42
15	V15		17.44
16	V16		17.08

*volumetric pigment content

From the polarization curves Ecorr - corrosion potential; Jcrt - critical corrosion current density were determined.

Results and discussion

The Bode and Nyquist diagrams obtained for electrodes coated iron V3, V7, V11 and V15 coatings polyester resins immersed in 3% NaCl solution are shown in **Figure 1**.

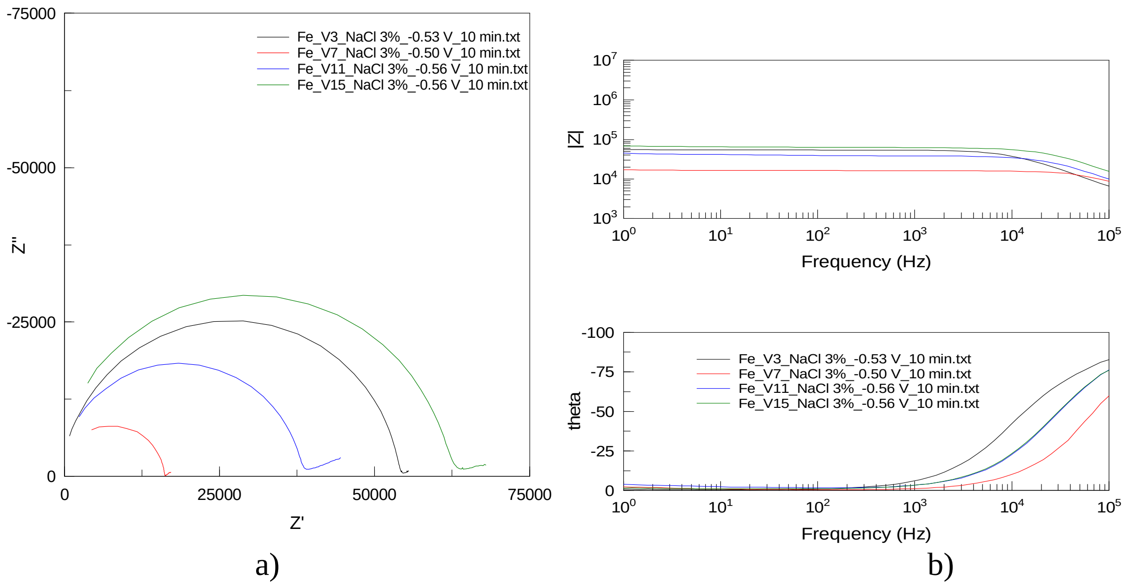

Figure 1. a) Nyquist diagram and b) Bode diagram (module of impedance and faze angle) for V3, V7, V11 and V15 coatings at 10 minute minute of imersion in 3% NaCl solution at OCP, V

Impedance spectra analysis revealed the presence of two time constants. A time constant due to the organic layer shaped by capacity - Cc and resistance of polymer film – Rp elements, capable to describes the dielectric and barrier properties of organic coating. The second time constant refers to the corrosion reactions and modeling / metal interface of the polymer film (capacity double layer - Cdl and charge transfer resistance - Rct). Comparing the impedance values of the coatings at the same VPC content, thickness and also exposure time, it was noted that they are dependent on the type of polyester resin.

The polarization resistance values obtained after modeling using equivalent electrical circuit for polymer films are between $10^4 \sim 10^6$ ohm cm $^{-2}$ and increase in general for the same type of resin with the increase of the volumetric pigment content (VPC %) (**Figure 2**).

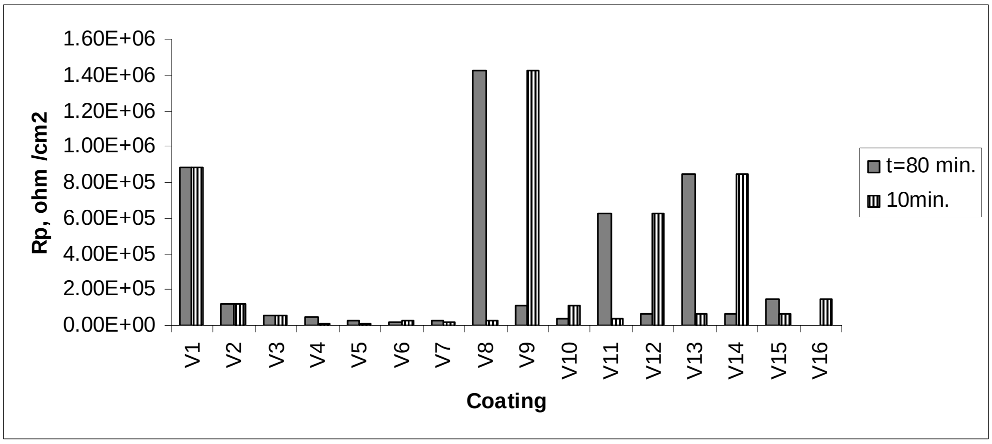

Figure 2. Variation of polarization resistance Rp with resine type for all coating formulation

The polarization resistance of polymer films shows that at a volumetric pigment concentration between 15-65 % it decreases in the order: resin R4 aliphatic polyurethane modified alkyd medium, followed by oil alkyd resin R1, R3 alkyd resin average modified styrene resin, R2 alkyd average modified aromatic polyurethane. For the same pigment concentration (25 %) is was observed that Rp is the maximum for resin R4, and at a lower concentration of pigment in resin type R3 (15%) allow to obtain a film with a higher Rp (**Figure 2**).

In time the coating capacitance (Cc) coating usually increases due to the water uptake as a result of the capillary action in the micro pore/defect structures. The volume fraction of water absorbed (W) can be calculated from coating capacitance (Cc) by equation (1) [4].

$$W = \frac{\log[C_t/C_0]}{\log 80} \quad (1)$$

where W is the volume fraction of the absorbed water, Ct is the coating capacitance at time t, C0 is the capacitance at t = 0, and 80 is the dielectric constant of water. In this investigation, the coating capacitance measured after 10 min. of immersion is taken as C_0 and after 80 min. of immersion as Ct. The water uptake are lower than 0.06 for all coatings and was observed that the fraction of water uptake decrease with de decrease of VPC in the formulation for R1 resin. For V7 respectively V15 the W presents the highest value. For the same VPC (15%), W is higher for R4 and pointed out that at lower VPC the W is affected substantially by resin type. R4 resin seams to be the less hydrophobic one. At a higher VPC (25%) the R1 resin is less hydrophobic. From potentiodynamic polarization curves the corrosion currents and corrosion rate were determined (**Figure 3**).

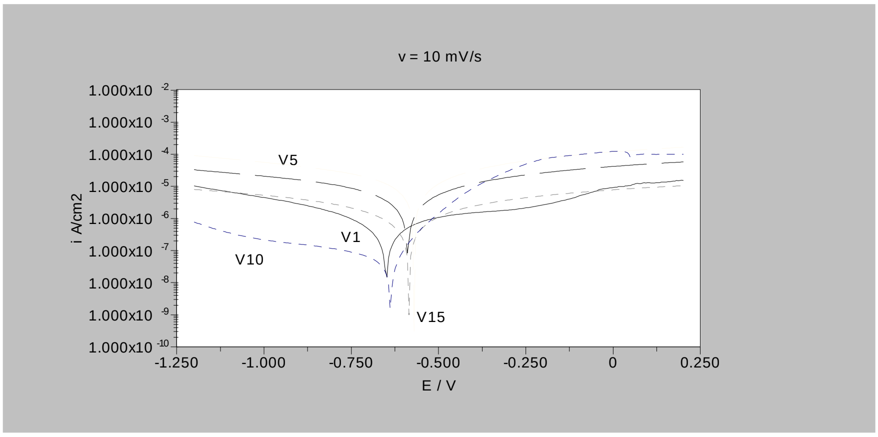

Figure 3. Potentiodynamic polarization curves for V1, V5, V10 and V15, scan rate 10 mV/s.

For R1 resin with 25-65 %VPC, R3 resin with 17-75 %VPC and R4 resin 17-47 % corrosion currents are lower. For a volumetric pigment concentration of 15 % and 20 % the lowest corrosion currents was obtained for resins R4. The corrosion rates, Rcorr determined from polarization curves for polyester films shows the same behavior observed for Rp data from EIS (**Figure 4**).

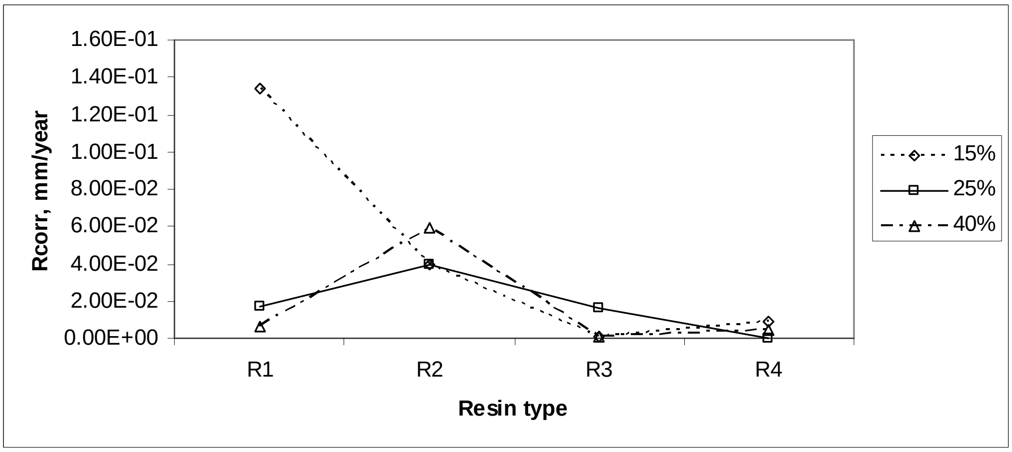

Figure 4. Corrosion rates (Rcorr) determined from polarization curve for different VPC

Conclusion

The corrosion rates decreases in the order: R4, followed by resin R3 and R1 and R2. For the same concentration of pigment, the corrosion rate is lower for films based on resin R4.

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